



Promoting effect of zirconium doping on Mn/ZSM-5 for the selective catalytic reduction of NO with NH₃

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HIGHLIGHTS

- ▶ The zirconium addition greatly enhances dispersion of active phases on the support surface.
- ▶ Additive of zirconium provides oxygen atoms a relatively free pathway for approaching the manganese atoms.
- ▶ The Mn–Zr/ZSM-5 catalyst exhibits higher activity than the Mn/ZSM-5 for selective catalytic reduction of NO with NH₃.

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ABSTRACT

Manganese–zirconium catalysts loaded on ZSM-5 (Si/Al = 25) were prepared using an ion-exchange method and investigated for the selective catalytic reduction of NO, with the aim of studying the effects of zirconium doping on the performance of Mn-based ZSM-5 catalysts. A series of characterization techniques, namely N₂-sorption, X-ray diffraction (XRD), scanning electron microscopy, transmission electron microscopy (TEM), temperature-programmed reduction by hydrogen, and X-ray photoelectron spectroscopy (XPS), were used to characterize these samples. TEM and XRD results showed that the addition of zirconium increased the manganese dispersion and prevented manganese crystallization. XPS results demonstrated that the introduction of zirconium enhanced the manganese species enrichment on the ZSM-5 grain surfaces. After zirconium addition, some of the manganese ions were incorporated into the zirconia lattice. The strong interaction between Mn and Zr contributed to the formation of Zr³⁺ ions or oxygen vacancies around the Zr⁴⁺ ions, which enhanced the redox abilities of the Mn–Zr/ZSM-5 catalysts. The temperature range for efficient NO conversion was lowered after zirconium doping. The MnZr3/ZSM-5 (Mn 3.2 wt.% and Zr 8.6 wt.%) sample exhibited NO_x conversions (>90%) over a wide temperature range (230–415 °C) and markedly superior to that of Mn/ZSM-5 (296–425 °C). Moreover, the formation of N₂O was suppressed at low temperatures due to the presence of zirconium in the catalysts.

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1. Introduction

Nitrogen oxides (NO_x) emitted from stationary sources and mobile diesel engines can be removed most effectively by the selective catalytic reduction (SCR) of NO_x by NH₃, using V₂O₅–WO₃/TiO₂ catalysts. However, these catalysts display certain disadvantages, such as a light-off temperature that is too high, a narrow operating temperature range, the formation of N₂O as a byproduct, and the toxicity of vanadium [1,2]. Also, the use of TiO₂ as a support is unsatisfactory because its poor specific surface area reduces the NO_x removal efficiency significantly [3]. Many research groups have therefore studied systems using other supports and active phases effective in the SCR of NO with NH₃ [4–6].

Recently, increased attention has been devoted to Mn/ZSM-5 catalysts [7–9]. Through ion-exchange procedures, manganese species are either anchored at ion-exchange sites to form isolated manganese ions via the lattice substituting for H⁺ at the bridging oxygen of Si–OH–Al groups, or enriched on the ZSM-5 surface to yield amorphous manganese oxides. The excellent catalytic performance arises largely from these isolated manganese ions and extra-framework manganese oxides [10,11]. Different combinations of manganese oxides (MnO, MnO₂, Mn₂O₃, and Mn₃O₄) can tailor the catalytic performance in different temperature ranges, thus broadening the activity window [11]. The volatile lattice oxygens generated in manganese oxides are beneficial in promoting the oxygen cycle and NH₃ activation [12].

Although the Mn/ZSM-5 catalyst exhibits good activity for the SCR of NO_x, its light-off temperature, >300 °C, is too high to cope with the cold-start and low-load working conditions of on-road

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Table 1
Elemental compositions of all catalysts.

Sample	Elemental composition measured by AAS (wt.%)			
	Mn	Zr	Al	Si
Pure ZSM-5	0	0	2.7	84.9
Mn/ZSM-5	3.1	0	2.6	79.7
MnZr1/ZSM-5	3.1	2.1	2.5	78.2
MnZr2/ZSM-5	3.2	5.2	2.4	75.6
MnZr3/ZSM-5	3.2	8.6	2.3	73.7
MnZr4/ZSM-5	3.2	11.2	2.1	70.2

Table 2
Physical and chemical properties of pure ZSM-5, Mn/ZSM-5 and Mn-Zr/ZSM-5 catalysts.

Sample	BET surface area ($\text{m}^2 \text{g}^{-1}$)	Micropore volume ($\text{cm}^3 \text{g}^{-1}$)
Pure ZSM-5	376	0.15
Mn/ZSM-5	351	0.13
MnZr1/ZSM-5	348	0.12
MnZr2/ZSM-5	330	0.12
MnZr3/ZSM-5	315	0.12
MnZr4/ZSM-5	267	0.11

engines. To further increase the low-temperature activity, it is necessary to introduce a second metal into the Mn/ZSM-5 as an additive [9]. The combination and interaction between the two metals have a significant effect on the bulk and surface physiochemical structure of Mn/ZSM-5 [13–15]. Zirconium is one of the most interesting metals for enhancing catalytic processes. Because of the presence of low-coordinated surface zirconium atoms, the embedding of zirconium into the framework of supporting materials causes variations in textural and surface features, and increases the deposition of active metal oxides [16]. These favorable characteristics provide opportunities for zirconium to be added as a second metal to monometallic catalysts [17,18]. Shi et al. [19] confirmed that Zr-promoted Pd/ZSM-5 catalysts possess high catalytic activity as well as thermal and hydrothermal stability for low-temperature methane combustion. A series of Mn–Zr mixed oxides was studied for the reduction of chlorocarbons by Gutiérrez-Ortiz et al. [20], who concluded that the higher activities obtained for Mn–Zr mixed oxides, compared with those obtained with pure Mn_2O_3 , was a result of their high acidities and readily accessible active oxygen species. Moreno-Tost et al. [21] found that in CuO_x -containing Zr-doped mesoporous silica catalysts for the SCR of NO by NH_3 , the excellent activity induced by zirconium addition can be correlated with the high dispersion of copper species and their redox properties.

In this work, a series of Mn–Zr/ZSM-5 catalysts was synthesized using a conventional ion-exchange method, and the effects of adding zirconium metal to Mn/ZSM-5 samples on the SCR activity of the catalysts for NO_x abatement were investigated using several techniques, namely N_2 sorption, X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and temperature-programmed reduction by hydrogen (H_2 -TPR). The results will be helpful in designing commercial molecular-sieve catalysts for diesel exhaust purification.

2. Experimental

2.1. Catalyst synthesis

In our previous study, the effects of Mn loading on ZSM-5 on the catalytic activity in SCR reactions were investigated [22]. The

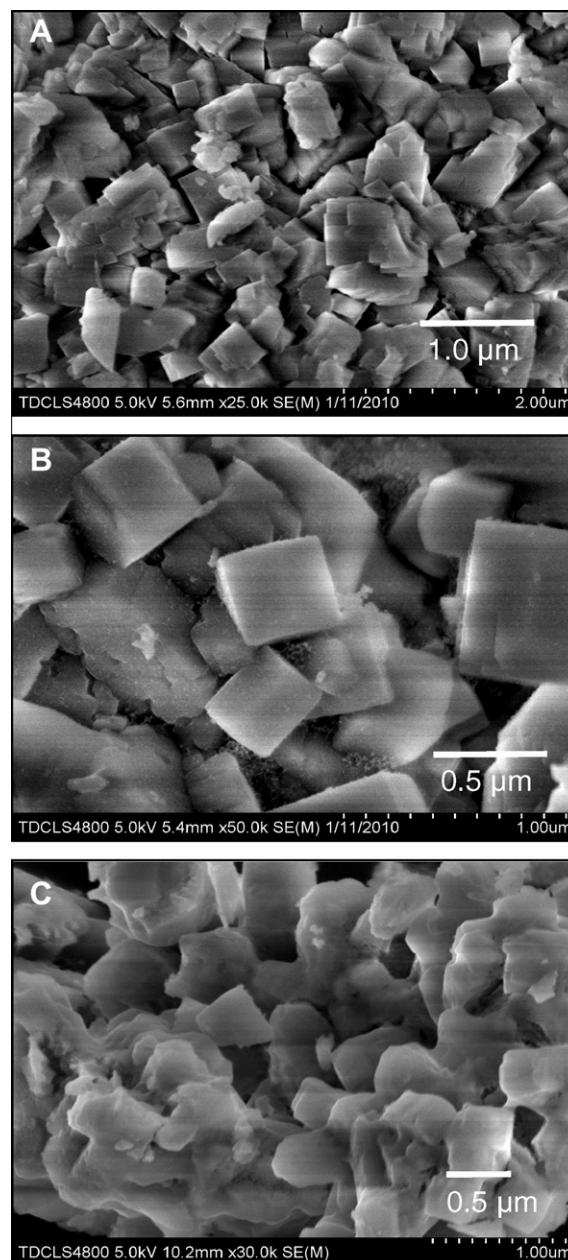


Fig. 1. Scanning electron microscopy images of (A) ZSM-5, (B) Mn/ZSM-5 and (C) MnZr3/ZSM-5.

optimum manganese content of Mn/ZSM-5 catalysts was approximately 3.1%. To better understand the effects of zirconium doping on Mn/ZSM-5, the manganese contents for all catalysts were fixed at 3.1% with a deviation of less than 3%. The Mn/ZSM-5 and Mn–Zr/ZSM-5 catalysts were prepared using a conventional ion-exchange method. H/ZSM-5 with an atomic Si/Al ratio of 25% and 100% crystallinity was supplied by Nankai University, Tianjin, China. Appropriate amounts of manganese and zirconium nitrates were dissolved in deionized water and mixed with 0.5 g of H/ZSM-5. The resulting solution was stirred at 80 °C for 24 h at a pH of approximately 7.0. After drying by evaporation, the sample was calcined in air at 550 °C for 4 h. The manganese and zirconium contents of each calcined catalyst were determined using atomic absorption spectrometry (AAS; AAnalyst 300, PerkinElmer, Waltham, MA, USA); the results are shown in Table 1. Prior to each catalytic activity test, the catalyst was pressed at a pressure of 20 MPa, and then granulated and screened to a size of 20–40 mesh.

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